

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of:

PFLUECKER, et al.:

Group Art Unit: 4162

Serial No.: 10/565,214

Examiner: Colette Nguyen

Filed: January 20, 2006

For: Nanoparticulate UV Protectant with Silicon Dioxide
Coating

DECLARATION UNDER 37 C.F.R. § 1.132

Assistant Commissioner for Patents
Alexandria, Virginia 22313-1450

SIR:

I, Bernd Hirthe, am a citizen of the Federal Republic of Germany residing at
Toenisvorst, Germany;

I am a chemical engineer by training and experience and I am inventor of the
pending patent application Serial No. 10/565,214.

I hereby declare that I supervised the following experiments:

Comparative data to the product according to Example 2d of the pending patent
application were created with two market products Maxlight TS-04® of Showa
Denko with 67% TiO₂ and 33 % Silica and Maxlight F-TS-20® of Showa Denko
with 80% TiO₂ and 20% Silica.

Comparative example 2e:

1 l of the aqueous hydrochloric acid suspension of TiO_2 from Example 1a (page 51) is brought to a pH of 9,0 using NaOH and heated to 80°C. 52 ml of water-glass solution (corresponding to 384 g of SiO_2/l) are subsequently added to the suspension. The pH arise to about pH 10,6. When the addition is complete, the pH is regulated by the addition of H_2SO_4 to pH 6,5 and the mixture is stirred at pH = 6,8 and 80°C for 2 hours. The product is subsequently washed to a conductivity of less than 100 $\mu\text{S}/\text{cm}$ and dried.

1. Photoactivity test – description of test system as of enclosure 1 to the declaration

Photoactivity-Test (Light Sensitive Color Difference)		dE*
Example 2d	Hydrothermal 180°C	2,0
Example 2e	Hydrothermal 105°C	16,5
Maxlight TS-04		7,6
Maxlight F-TS20		5,5

Photoactivity-Test (Light Sensitive Color Difference)

Receipe: Formulation BCI

Irradiation: 1h 765W/m² (ATLAS Suntest CPS+)

Measurement: L*a*b* (Kollmorgen CE7000)

Formula: $\Delta E^* = [(L^*_{\text{after}} - L^*_{\text{before}})^2 + (a^*_{\text{after}} - a^*_{\text{before}})^2 + (b^*_{\text{after}} - b^*_{\text{before}})^2]^{1/2}$

The inventive TiO_2 according to example 2d has significantly better dE-values in comparison to the other products which mean that the greying of the products is decreased.

Another effect of the hydrothermal treatment is the displacement of the UV absorption to UV A absorption.

2. Better UV A absorption in a clear coat

The test system is described in enclosure 2 to the declaration

Results:

	max. Absorption / Extinction
Hydrothermal treatment at 105°C	286 nm
Hydrothermal treatment at 150°C	294 nm
Hydrothermal treatment at 180°C	300 nm
Hydrothermal treatment at 225°C	304 nm

The shift to higher wavelength of the max. absorption leads to better UV-A protection and to better UV-A/UV-B ratio.

Although less likely than UVB to cause sunburn, UVA penetrates the skin more deeply, and is considered the chief culprit behind wrinkling, leatherying, and other aspects of "photoaging." The latest studies show that UVA not only increases UVB 's cancer-causing effects, but may directly cause some skin cancers, including melanomas.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date:

16.10.2008



Bernd Hirthe

Determination of the light stability of fine particled titanium dioxide in cosmetic emulsions

Basis

If emulsions containing titanium dioxide are exposed to UV radiation it is possible to determine an undesired greying of the emulsion to a greater or lesser extent. The extent of greying depends on the light stability of the titanium dioxide sample incorporated.

Apparatus and reagents

1. Sample plate, plastic (own production)
2. Quartz glass plates
3. Colour measurement device (e.g. Kollmorgen CE7000)
4. Source of irradiation: SUNTESTCPS+, with Solar Standard Filter from ATLAS

Method

The BCI cosmetic emulsion containing titanium dioxide is poured into the sample plate [1]. The emulsion is covered over with a quartz glass plate [2] in order to preclude air contact. The unexposed sample is then measured using a colour measurement device [3] (illuminant C, 2° normal observer).

The sample plate is placed in the centre of the irradiation area of the SUNTESTCPS+ [4] and the irradiation chamber is closed. The sample is irradiated for 30 minutes at 765 W/m², the irradiation process is then interrupted by opening the irradiation chamber and the sample immediately measured using the colour measurement device [3].

Subsequently irradiation continues at the same strength for a further 30 minutes, and new measurements are recorded.

Evaluation

The lab* values are calculated from the measured values (analogue DIN 6174).

Calculation: $\Delta E^* = [(L^*_{\text{after}} - L^*_{\text{before}})^2 + (a^*_{\text{after}} - a^*_{\text{before}})^2 + (b^*_{\text{after}} - b^*_{\text{before}})^2]^{1/2}$

Manufacturing of the BCI cosmetic emulsion containing titanium dioxide

Apparatus

- (1) Heater
- (2) Microwave
- (3) Dispermatc;V disperser (from VMA Getzmann), toothed disc 0 2.5 cm
- (4) Ultra Turrax T 25 (from IKA), dispersal tool S25N-25F
- (5) Thermometer
- (6) 150 ml beaker
- (7) 100 ml beaker

Chemicals

- | | | |
|-----|------------------------------|-----------------------------------|
| [1] | Dimethicone, viscosity 50 cs | e.g. Dow Corning 200 FLuid 50 cs, |
| [2] | Elfacos ST9 | from Akzo |
| [3] | Elfacos C26 | from Akzo |

[4]	DL-alpha tocopherol acetate	e.g. from Merck, Order No. 500952
[5]	Octyl Palmitate	e.g. Crodamol OP, from Croda
[6]	Dow Corning 345 Fluid	from Dow Corning
[7]	Glycerine DAB	e.g. from Merck, Order No. 4093
[8]	Germaben II-E	from ISP Global Technologies
[9]	Demineralised water	

Oil phase

3 g	Dimethicone [1]
10.8 g	Elfacos ST9 [2]
5.4 g	Elfacos C26 [3]
1 g	DL-alpha tocopherol acetate [4]
6 g	DC 345 Fluid [6]
5 g	TiO ₂ to be examined
21.8 g	Octyl Palmitate [5]

Water phase

36 g	demineralised water [9]
5 g	Glycerine DAB [7]

Preservative

1 g	Germaben II-E [8]
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Preparation of the oil phase

The constituents of the oil phase apart from DC 345 Fluid [6] and the powder material to be examined are weighed and placed in a beaker (6) and stirred while being heated to 60 °C (heater (1)). Once the constituents have dissolved, the DC Fluid 345 [6] is added. Using the disperser (3), the TiO₂ powder is dispersed into the oil phase. During dispersal the temperature in the beaker is kept at 60 °C with the aid of the heater (1).

Preparation of the water phase

The constituents [9] and [7] are weighed into a beaker (7) and stirred while being heated to 60 °C (heater (1) or microwave (2)).

Preparation of the emulsion

While stirring well using the disperser (3), the water phase which is at a temperature of 60 °C into the oil phase which similarly has a temperature of 60 °C, and stirred for around another 60 sec. After the emulsion has cooled to 25 – 35 °C, the preservative Germaben II-E [8] is added. The emulsion is homogenised for three minutes at 13,500 rpm⁻¹ using the Ultra Turrax (4).

Description of the preparation of surface finishes to determine transmission spectra

Preparation of the finishes :

1. Milling paste with sample

Macrynal SM 510 n	36.30g
Xylol/MPA 2:1	43.27g
Product	42.00g
Total	121.25g

All constituents are weighed to an accuracy of 0.05g into a 300 ml wide-necked Kautex bottle and displaced with 300 g (+/- 3g) of glass beads (diameter 2mm). After briefly shaking by hand (approx. 10 sec), the Kautex bottles are clamped in the Skandex and shaken for 90 min.

2. Auxiliary solution

Mark DBTL (1% concentration in Xylol)	0.94g
Diethylethanolamine	1.68g
Silicone oil L 050	4.41g
Solvesso 100	24.67g
Xylol	28.64g
Methoxypropylacetate	39.66g
Total	100.0g

All constituents are homogenised.

3. Formula for coating

Macrynal SM 510 n	39.90g
Milling paste sample (see below)	2.00g
Desmodur N 75	17.21g
Auxiliary solution (see below)	19.74g
Xylol/MPA 2:1	21.15g
Total	100.00g

To prepare the test coatings the milling paste (1) is manually applied in the quantities stipulated under (3) by stirring.

Determination of the UV absorption

The applied milling paste (3rd coating formulation) is applied to a 125µm thick acetate foil with a spiral scraper (60µm). After a cooling period of 5 min the coating is force dried at 80 °C for around 30 min.

The extinction measurement takes place using transmission to a UV-Vis spectrometer (Ulbricht sphere) with luminant D65.

Trade name	Chemical composition	Manufacturer
Macrynal SM 510 n	Acrylate bonding agent	Cytec Surface Specialties
MPA	Methoxypropylacetate	Laboratory products
Mark DBTL	Dibutyl tin (IV) dilaurate	Crompton Vinyl Additives GmbH
-	Diethylethanolamine	Laboratory products
Silicon oil L 050	-	Wacker Chemie
Solvesso 100	-	Exxon Mobile Chemical
-	Dimethylbenzene (Xylol)	Laboratory products
-	Methoxypropylacetate	Laboratory products
Desmodur N 75	Isocyanate bonding agent	Bayer